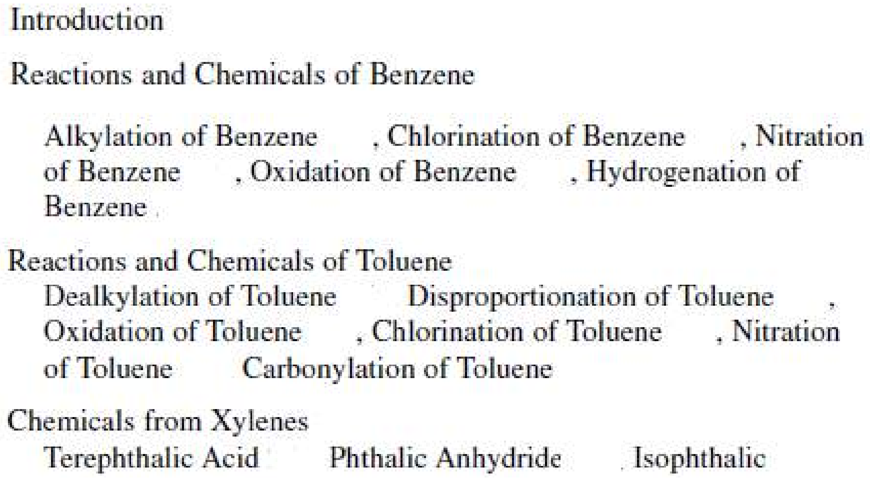
Chapter 6: Aromatics Production



Introduction

Reactions and Chemicals of Benzene

Alkylation of Benzene , Chlorination of Benzene , Nitration of Benzene , Oxidation of Benzene , Hydrogenation of Benzene

Reactions and Chemicals of Toluene

Dealkylation of Toluene Disproportionation of Toluene , Oxidation of Toluene , Chlorination of Toluene , Nitration of Toluene Carbonylation of Toluene

Chemicals from Xylenes

Terephthalic Acid Phthalic Anhydride Isophthalic

6.1 INTRODUCTION

The primary sources of benzene, toluene, and xylenes (BTX) are refinery streams, especially from catalytic reforming and cracking, and pyrolysis gasoline from steam cracking and from coal liquids. BTX and ethyl benzene are extracted from these streams using selective solvents such as sulfolene or ethylene glycol. The extracted components are separated through lengthy fractional distillation, crystallization, and isomerization processes.

The reactivity of C_6, C_7, C_8 aromatics is mainly associated with the benzene ring. Aromatic compounds in general are liable for electrophilic substitution. Most of the chemicals produced directly from benzene are obtained from its reactions with electrophilic reagents. Benzene could be alkylated, nitrated, or chlorinated to important chemicals that are precursors for many commercial products.

Toluene and xylenes (methylbenzenes) are substituted benzenes. Although the presence of methyl substituents activates the benzene ring for electrophilic attack, the chemistry of methyl benzenes for producing commercial products is more related to reactions with the methyl than with the phenyl group. The methyl group could be easily oxidized or chlorinated as a result of the presence of the phenyl substituent.

6.2 REACTIONS AND CHEMICALS OF BENZENE

Benzene (C_6H_6) is the most important aromatic hydrocarbon. It is the precursor for many chemicals that may be used as end products or intermediates. Almost all compounds derived directly from benzene are converted to other chemicals and polymers. For example, hydrogenation of benzene produces cyclohexane. Oxidation of cyclohexane produces cyclohexanone, which is used for nylon manufacture. Due to the resonance stabilization of the benzene ring, it is not easily polymerized.

However, products derived from benzene such as styrene, phenol, and maleic anhydride can polymerize to important commercial products due to the presence of reactive functional groups. Benzene could be alkylated by different alkylating agents, hydrogenated to cyclohexane, nitrated, or chlorinated.

6.2.1 Alkylation of Benzene

Benzene can be alkylated in the presence of a Lewis or a Bronsted acid catalyst. Olefins such as ethylene, propylene, and C_{12}–C_{14} alpha olefins are used to produce benzene alkylates, which have great commercial value.

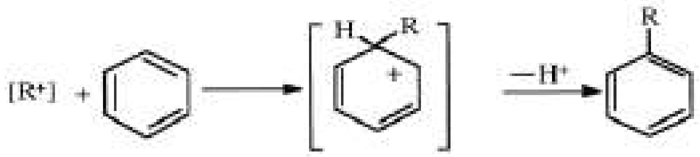
The first step in alkylation is the generation of a carbonium ion, and when an olefin is the alkylating agent, a carbonium ion intermediate forms.

$$RCH{=}CH_2 \xrightarrow{H^+} [R\overset{+}{C}HCH_3]$$

Carbonium ions also form from an alkyl halide when a Lewis acid catalyst is used. Aluminum chloride is the commonly used Friedel-Crafts alkylation catalyst:

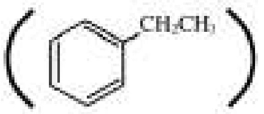
$$RCl + AlCl_3 \rightarrow [R^+ \_\_\_\_ AlCl_4^-]$$

The next step is an attack by the carbonium ion on the benzene ring, followed by the elimination of a proton and the formation of benzene alkylate:



6.2.2 Important chemicals based on benzene

Ethylbenzene (EB)



Ethylbenzene (EB) is a colorless aromatic liquid with a boiling point of 136.2°C, very close to that of p-xylene. This complicates separating it from the C_8 aromatic equilibrium mixture obtained from catalytic reforming processes. Ethylbenzene obtained from this source, however, is small compared to the synthetic route. The main process for producing EB is the catalyzed alkylation of benzene with ethylene:

In the liquid-phase reaction over $AlCl_3$ catalyst, the conditions of the process are 40-100°C and 2-8 atmospheres. Diethylbenzene and higher alkylated benzenes also form. They are recycled and dealkylated to EB.

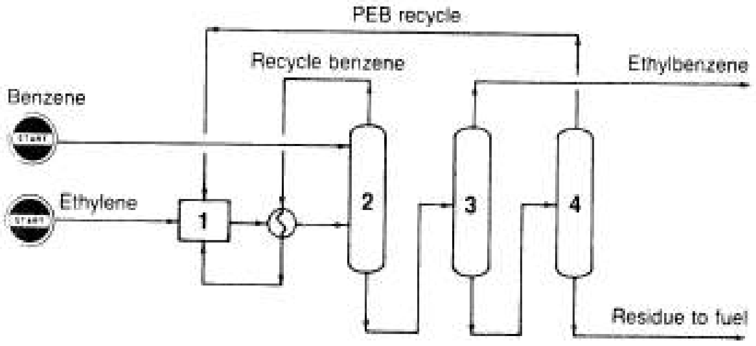
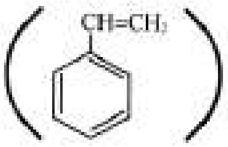


Figure 6-1 The Badger process for producing ethylbenzene: (1) reactor, (2) fractionator (for recovery of unreacted benzene), (3) EB fractionator, (4) polyethylbenzene recovery column.

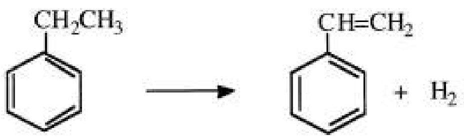
Description

The vapor-phase Badger process (Figure 6-1), which has been commercialized since 1980, zeolite type heterogeneous catalyst is used in a fixed bed process. The reaction conditions are 420°C and 13-20 atm. Over 98% yield is obtained at 90% conversion.4,5 Polyethylbenzene (PEB) and unreacted benzene are recycled and join the fresh feed to the reactor. The reactor effluent is fed to the benzene fractionation system to recover unreacted benzene. The bottoms containing ethylbenzene and heavier PEB are fractionated in two columns. The first column separates the ethylbenzene product, and the other separates polyethylbenzene for recycling.

Styrene



Styrene (vinylbenzene) monomer is a liquid (b.p. 145.2°C) that polymerizes easily when initiated by a free radical or when exposed to light. Dehydrogenation of ethylbenzene (EB) to styrene occurs over a wide variety of metal oxide catalysts.



Oxides of Fe, Cr, Si, Co, Zn, or their mixtures can be used for the dehydrogenation reaction. Typical reaction conditions for the vapor-phase process are 600-700°C, at or below atmospheric pressure. Approximately 90% styrene yield is obtained of 30-40% conversion:

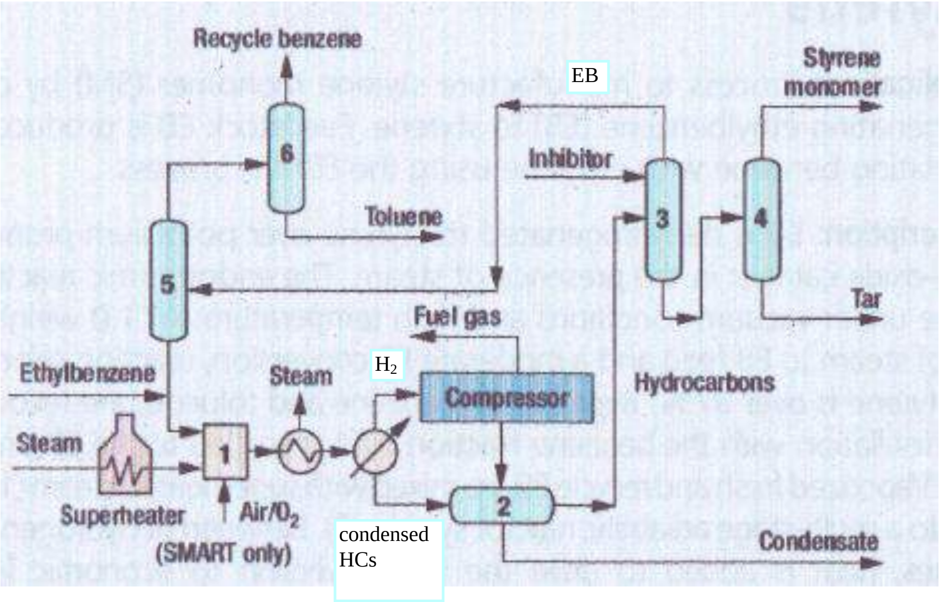
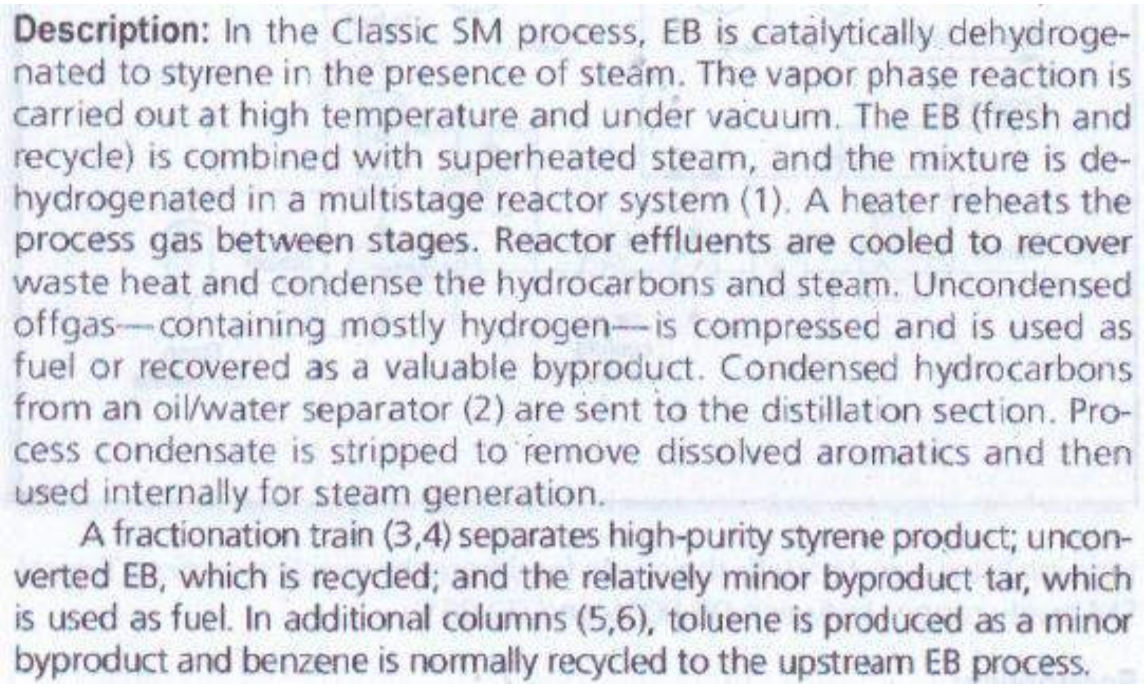


Figure 6-3 Dehydrogenation of ethylbenzene (EB) using the Lummus/UOP smart for Styrene plant



Description: In the Classic SM process, EB is catalytically dehydrogenated to styrene in the presence of steam. The vapor phase reaction is carried out at high temperature and under vacuum. The EB (fresh and recycle) is combined with superheated steam, and the mixture is dehydrogenated in a multistage reactor system (1). A heater reheats the process gas between stages. Reactor effluents are cooled to recover waste heat and condense the hydrocarbons and steam. Uncondensed offgas—containing mostly hydrogen—is compressed and is used as fuel or recovered as a valuable byproduct. Condensed hydrocarbons from an oil/water separator (2) are sent to the distillation section. Process condensate is stripped to remove dissolved aromatics and then used internally for steam generation.

A fractionation train (3,4) separates high-purity styrene product; unconverted EB, which is recycled; and the relatively minor byproduct tar, which is used as fuel. In additional columns (5,6), toluene is produced as a minor byproduct and benzene is normally recycled to the upstream EB process.

The effect of steam/EB ratio, temperature, and pressure on the equilibrium conversion of EB is shown in Figure 6-4.

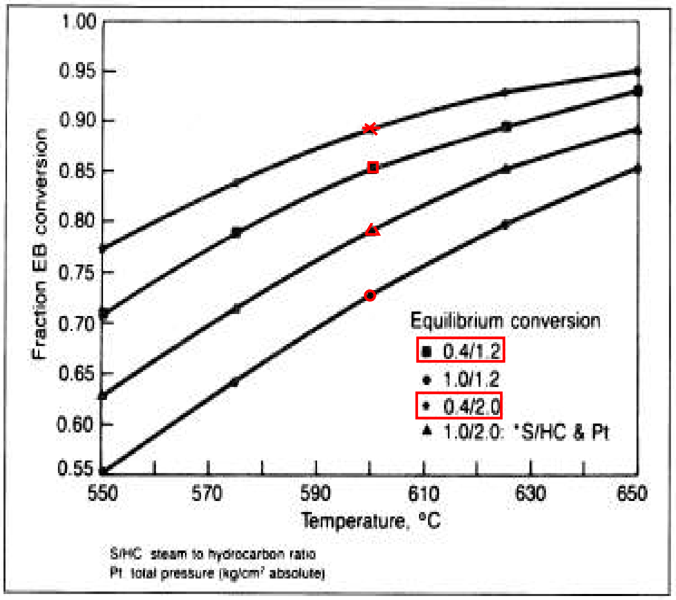
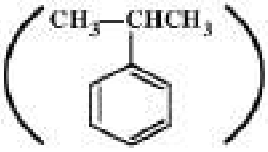
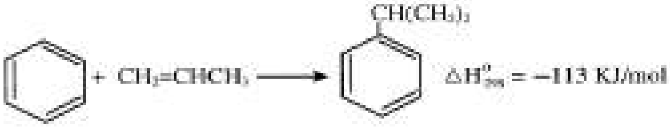


Figure 6-4 Effect of steam/EB, temperature, and pressure on the conversion of ethylbenzene

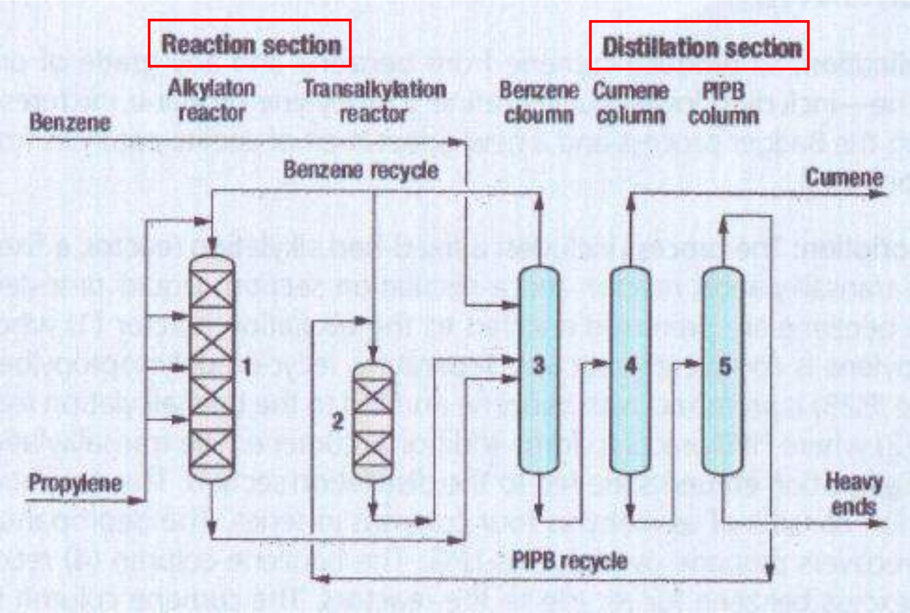
Cumene



Cumene (isopropylbenzene), a liquid (B.P. is 152.7°C) is soluble in many organic solvents but not in water. It is present in low concentrations in light refinery streams (such as reformates) and coal liquids. It may be obtained by distilling these fractions. The main process for producing cumene is a synthetic route where benzene is alkylated with propylene to isopropylbenzene. Either a liquid or a gas-phase process is used for the alkylation reaction.



In the liquid-phase process, low temperatures and pressures (50°C and 5 atm.) are used with zeolite catalyst.

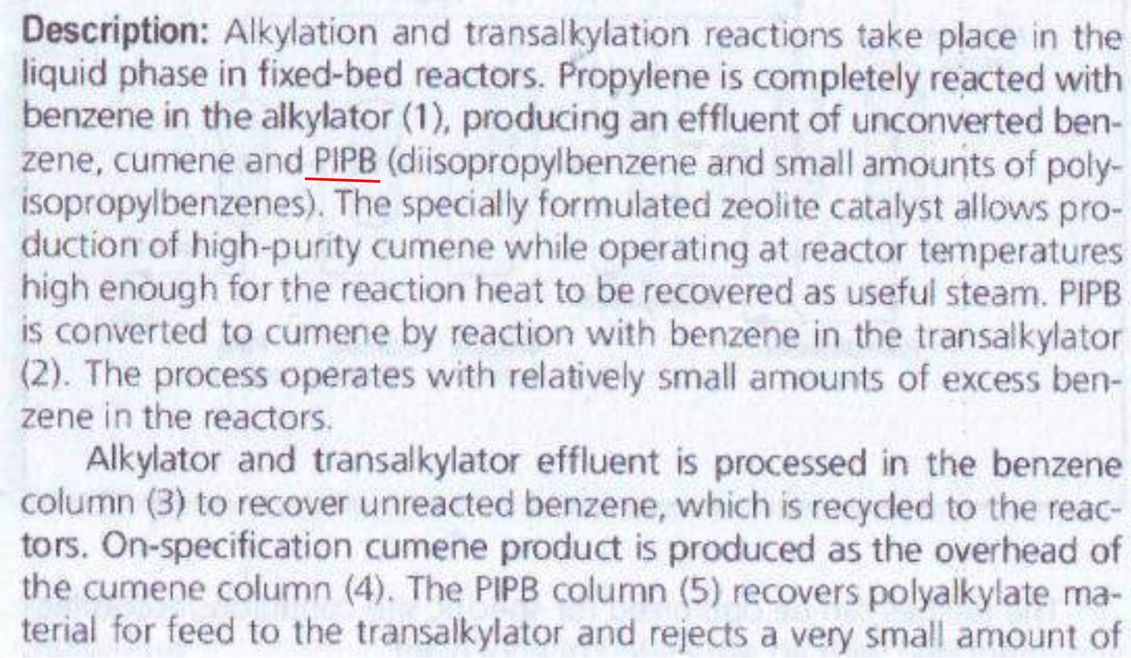


Alkylation is a process which combines olefins (primarily a mixture of propylene and butylene) with Bz in the presence of a catalyst

Transalkylation is a chemical reaction involving the transfer of propyl group from PIPB compound to Bz in the presence of a catalyst

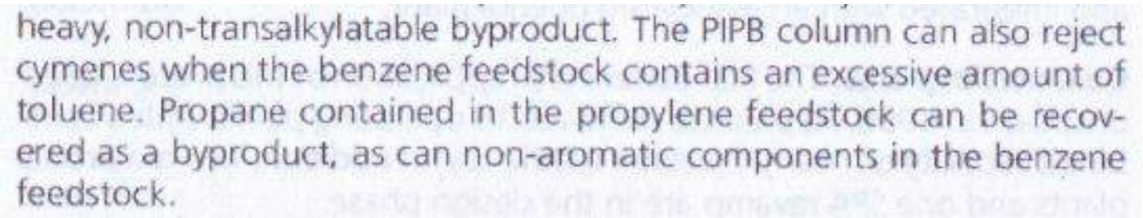
Figure 6-5 The Polimeri/Lummus process to produce high purity cumene from propylene and benzene

PIPB, diisopropyl-benzene and triisopropylbenzene



Description: Alkylation and transalkylation reactions take place in the liquid phase in fixed-bed reactors. Propylene is completely reacted with benzene in the alkylator (1), producing an effluent of unconverted benzene, cumene and PIPB (diisopropylbenzene and small amounts of polyisopropylbenzenes). The specially formulated zeolite catalyst allows production of high-purity cumene while operating at reactor temperatures high enough for the reaction heat to be recovered as useful steam. PIPB is converted to cumene by reaction with benzene in the transalkylator (2). The process operates with relatively small amounts of excess benzene in the reactors.

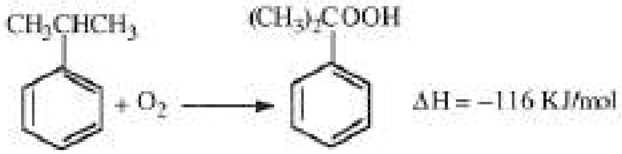
Alkylator and transalkylator effluent is processed in the benzene column (3) to recover unreacted benzene, which is recycled to the reactors. On-specification cumene product is produced as the overhead of the cumene column (4). The PIPB column (5) recovers polyalkylate material for feed to the transalkylator and rejects a very small amount of



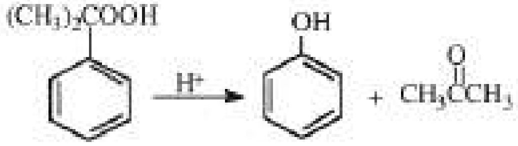
heavy, non-transalkylatable byproduct. The PIPB column can also reject cymenes when the benzene feedstock contains an excessive amount of toluene. Propane contained in the propylene feedstock can be recovered as a byproduct, as can non-aromatic components in the benzene feedstock.

Phenol and Acetone from Cumene

Cumene process is currently the major source for phenol and co-product acetone. Phenol, C_6H_5OH (hydroxybenzene), is produced from cumene by a two-step process. In the first step, cumene is oxidized with air to cumene hydroperoxide. The reaction conditions are approximately 100-130°C and 2-3 atm. in the presence of a metal salt catalyst:



In the second step, the hydroperoxide is decomposed in the presence of an acid to phenol and acetone. The reaction conditions are approximately 80°C and slightly below atmospheric:



Description

In this process (Fig. 6-6) cumene is oxidized (1) with air in the liquid phase to produce cumene hydroperoxide 80% and concentrated under vacuum distillation (2). To avoid decomposition of the hydroperoxide, it is transferred immediately to the cleavage reactor (3) in the presence of a small amount of H_2SO_4. The cleavage product is neutralized with alkali before fractionation (5-8) to produce high purity products.

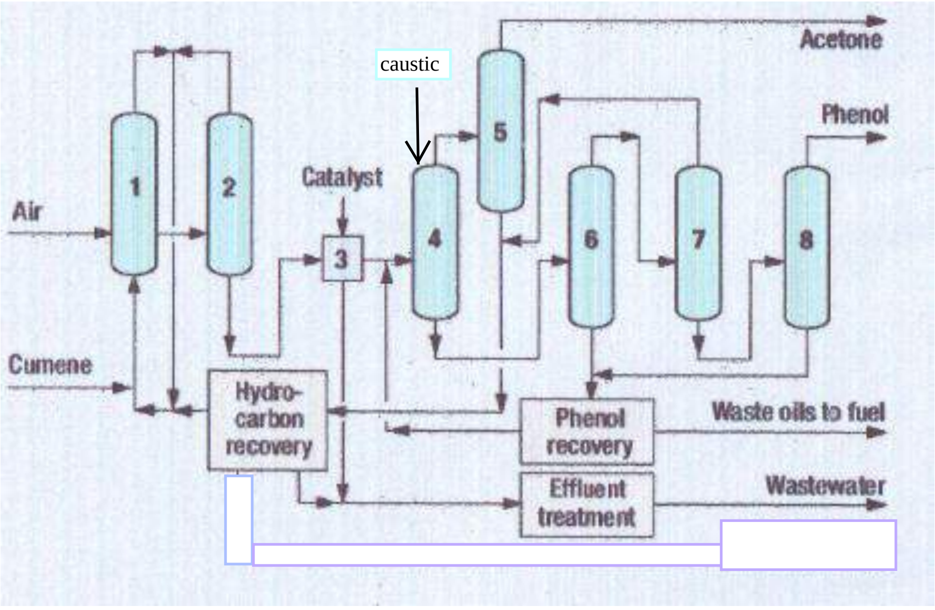


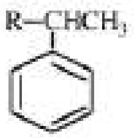
Figure 6-6. The Kellogg Brown & Root process for producing phenol and acetone from cumene: (1) auto-oxidation reactor, (2) vacuum distillation tower, (3) cleavage reactor, (4) neutralizer, (5–8) purification train.

After an initial distillation to split the co-products phenol and acetone, each is purified in separate distillation and treating trains. An acetone finishing column distills product acetone from an acetone/water/oil mixture. The oil, which is mostly unreacted cumene, is sent to cumene recovery. Acidic impurities, such as acetic acid and phenol, are neutralized by caustic injection.

Properties and Uses of Phenol

Phenol, a white crystalline mass with a distinctive odor, becomes reddish when subjected to light. It is highly soluble in water, and the solution is weakly acidic. Phenol was the 3rd highest-volume chemical. Many chemicals and polymers derive from phenol. Approximately 50% of production goes to phenolic resins. Phenol and acetone produce bis-phenol, salicylic acid, acetylsalicyclic acid (aspirin), 2,4-dichlorophenoxy acetic acid (2,4-D), and 2,4,5- triphenoxy acetic acid (2,4,5-T), which are selective herbicides; and pentachlorophenol, a wood preservative.

Linear Alkylbenzene



Linear alkylbenzene (LAB) is an alkylation product of benzene used to produce biodegradable anionic detergents. The alkylating agents are either linear C_{12}–C_{14} mono-olefins or monochloroalkanes. The linear olefins (alpha olefins) are produced by dehydrogenating n-paraffins extracted from kerosene. The dehydrogenation of n-paraffins to mono-olefins was occurred with a newly developed dehydrogenation Ziegler catalyst.

Principle

The process (Figure 6-7) combines the dehydrogenation of n-paraffins and the alkylation of benzene. Mono-olefins from the dehydrogenation section are introduced to a fixed-bed alkylation reactor over a heterogeneous solid catalyst. Alkylation of benzene with linear mono-olefins is industrially preferred in a liquid phase process at a temperature range of 40-70°C. The feedstock is typically C_{10}-C_{13} normal parrafin of 98% purity.

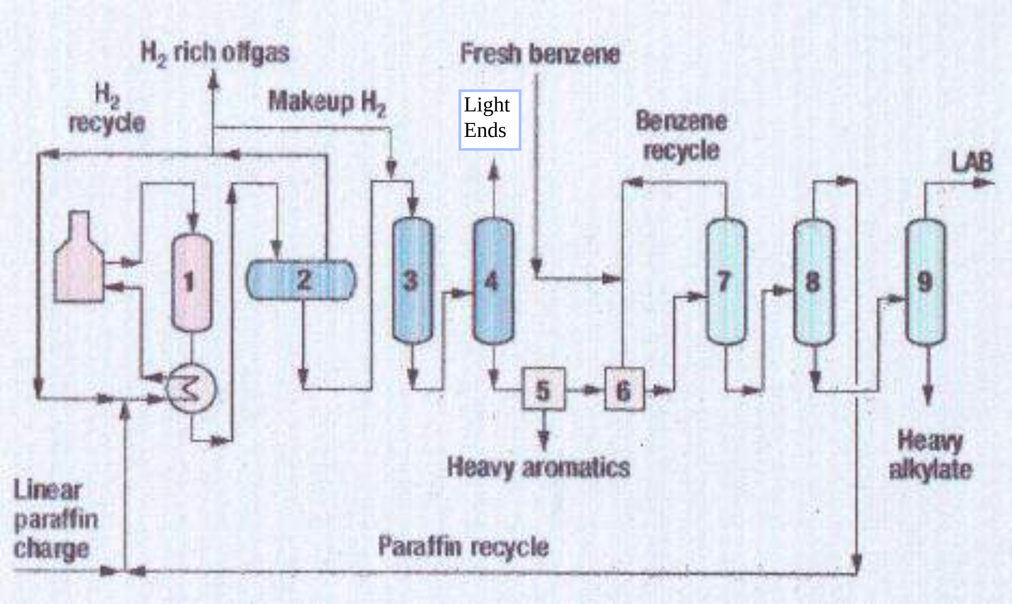
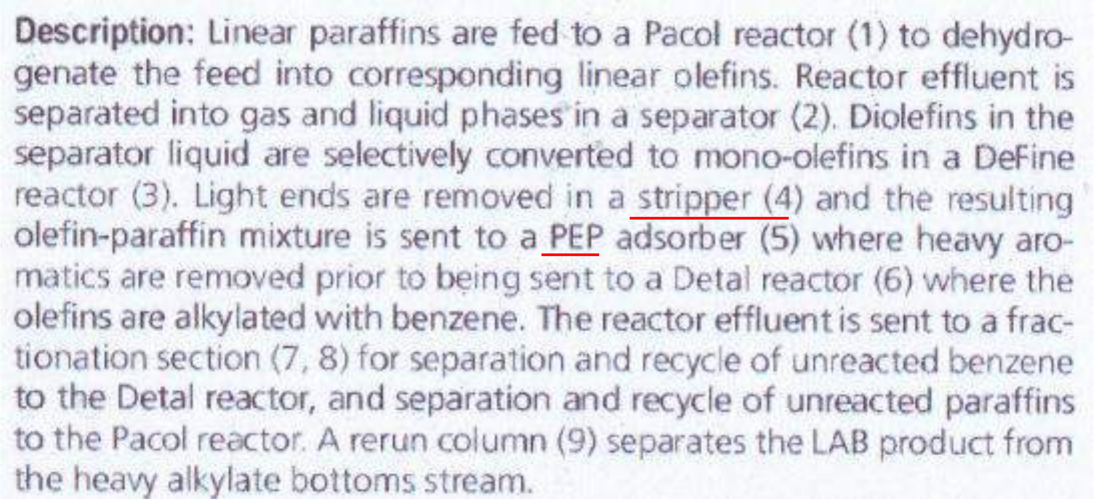


Figure 6-7 The UOP/CEPSA process for producing linear alkylbenzene

The general alkylation reaction of benzene using alpha olefins could be represented as:

Linear alkylbenzene (LAB)

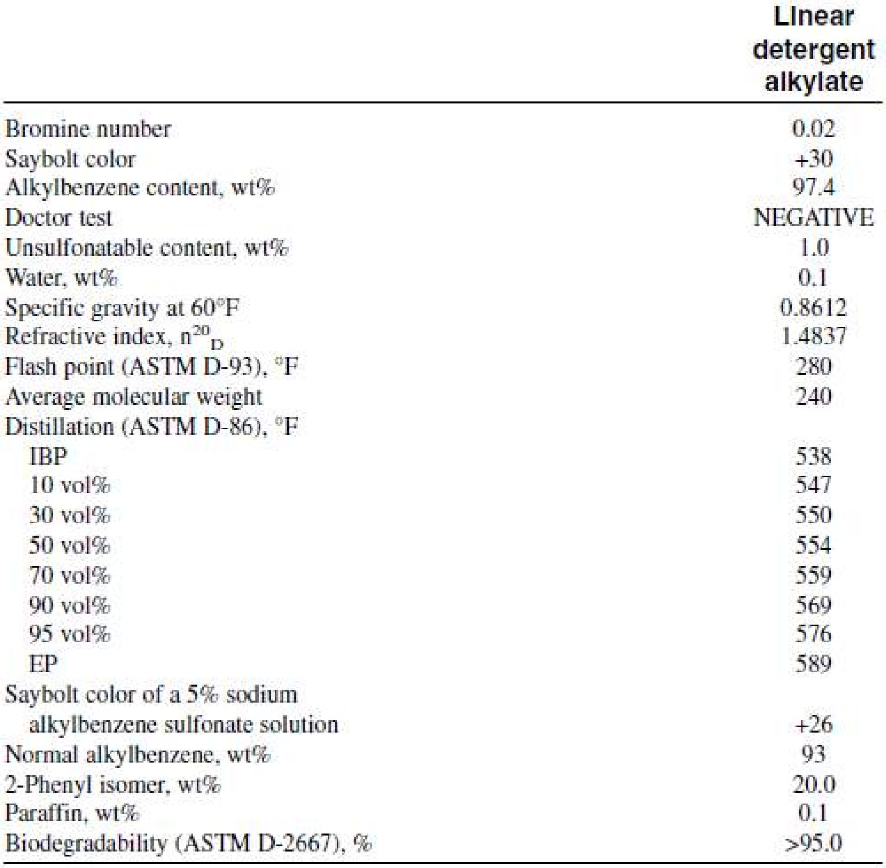
Paraffin Extraction Process



Description: Linear paraffins are fed to a Pacol reactor (1) to dehydrogenate the feed into corresponding linear olefins. Reactor effluent is separated into gas and liquid phases in a separator (2). Diolefins in the separator liquid are selectively converted to mono-olefins in a DeFine reactor (3). Light ends are removed in a stripper (4) and the resulting olefin-paraffin mixture is sent to a PEP adsorber (5) where heavy aromatics are removed prior to being sent to a Detal reactor (6) where the olefins are alkylated with benzene. The reactor effluent is sent to a fractionation section (7, 8) for separation and recycle of unreacted benzene to the Detal reactor, and separation and recycle of unreacted paraffins to the Pacol reactor. A rerun column (9) separates the LAB product from the heavy alkylate bottoms stream.

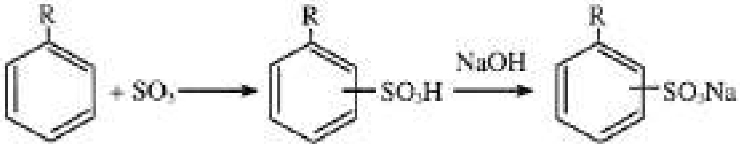
A typical properties of detergent alkylate are shown in Table 6-1.

Table 6-1 Typical properties of detergent alkylate.



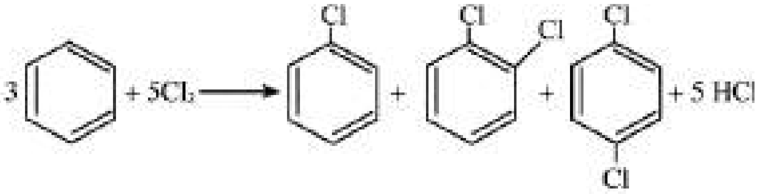
	Linear detergent alkylate
Bromine number	0.02
Saybolt color	+30
Alkylbenzene content, wt%	97.4
Doctor test	NEGATIVE
Unsulfonatable content, wt%	1.0
Water, wt%	0.1
Specific gravity at 60°F	0.8612
Refractive index, n^{20}_D	1.4837
Flash point (ASTM D-93), °F	280
Average molecular weight	240
Distillation (ASTM D-86), °F	
IBP	538
10 vol%	547
30 vol%	550
50 vol%	554
70 vol%	559
90 vol%	569
95 vol%	576
EP	589
Saybolt color of a 5% sodium alkylbenzene sulfonate solution	+26
Normal alkylbenzene, wt%	93
2-Phenyl isomer, wt%	20.0
Paraffin, wt%	0.1
Biodegradability (ASTM D-2667), %	>95.0

Detergent manufacturers buy linear alkylbenzene, sulfonate with SO_3, and then neutralize it with NaOH to produce linear alkylbenzene sulfonate (LABS), the active ingredient in detergents:



6.2.3 **Chlorination of Benzene**

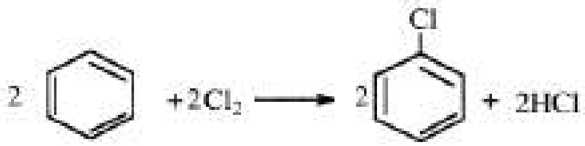
Chlorination of benzene is an electrophilic substitution reaction in which Cl^+ serves as the electrophile. The reaction occurs in the presence of Lewis acid catalyst such as $FeCl_3$. The products are a mixture of mono- and dichlorobenzenes. The *ortho*- and the *para*-dichlorobenzenes are more common than meta-dichlorobenzene. The ratio of the monochloro to dichloro products essentially depends on the benzene/chlorine ratio and the residence time. The ratio of the dichloro-isomers (o- to p- to m-dichlorobenzenes) mainly depends on the reaction temperature and residence time:



Typical liquid-phase reaction conditions for the chlorination of benzene using $FeCl_3$ catalyst are 80-100°C and atmospheric pressure. When a high benzene/Cl_2 ratio is used, the product mixture is approximately 80% monochlorobenzene, 15% p-dichlorobenzene and 5% o-dichlorobenzene.

Continuous chlorination processes permit the removal of monochlorobenzene as it is formed, resulting in lower yields of higher chlorinated benzene. Monochlorobenzene is also produced in a vapor-phase process at approximately 300°C. The by-product HCl goes into a regenerative oxychlorination reactor. The catalyst is a promoted copper oxide on a silica carrier:

$$4\,HCl + O_2 \longrightarrow 2\,Cl_2 + 2\,H_2O$$



Higher conversions have been reported when temperatures of 234-315°C and pressures of 40-80 psi are used.

Uses: Monochlorobenzene is the starting material for many compounds, including phenol and aniline. Others such as DDT, chloronitrobenzenes, polychlorobenzenes, and biphenyl.

6.2.4 **Nitration of Benzene**

Nitrobenzene [$C_6H_5NO_2$]

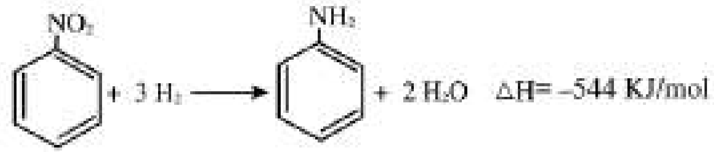
Similar to the alkylation and the chlorination of benzene, the nitration reaction is an electrophilic substitution of benzene hydrogen (H^+) with a nitronium ion (NO^{+2}). The liquid-phase reaction occurs in presence of both concentrated nitric and sulfuric acids at approximately 50°C. Concentrated sulfuric acid has two functions: it reacts with nitric acid to form the nitronium ion, and it absorbs the water formed during the reaction, which shifts the equilibrium to the formation of nitrobenzene:

$$HNO_3 + 2H_2SO_4 \longrightarrow 2\ HSO_4^- + H_3O^+ + NO_2^+$$

Most of the nitrobenzene (≈97%) produced is used to make aniline. Other uses include synthesis of quinoline, benzidine, and as a solvent for cellulose ethers.

Aniline ($C_6H_5NH_2$)

Aniline (aminobenzene) is an oily liquid that turns brown when exposed to air and light. The compound is an important dye precursor. The main process for producing aniline is the hydrogenation of nitrobenzene:



The hydrogenation reaction occurs at approximately 270°C and slightly above atmospheric over a Cu/Silica catalyst. About a 95% yield is obtained.

2 Ammonolysis of phenol occurs in the vapor phase.

Description

In the Scientific Design Co. process (Figure 6-8), a mixed feed of ammonia and phenol is heated and passed over a heterogeneous catalyst in a fixed-bed system. The reactor effluent is cooled, the condensed material distilled, and the unreacted ammonia recycled. Aniline produced this way should be very pure:

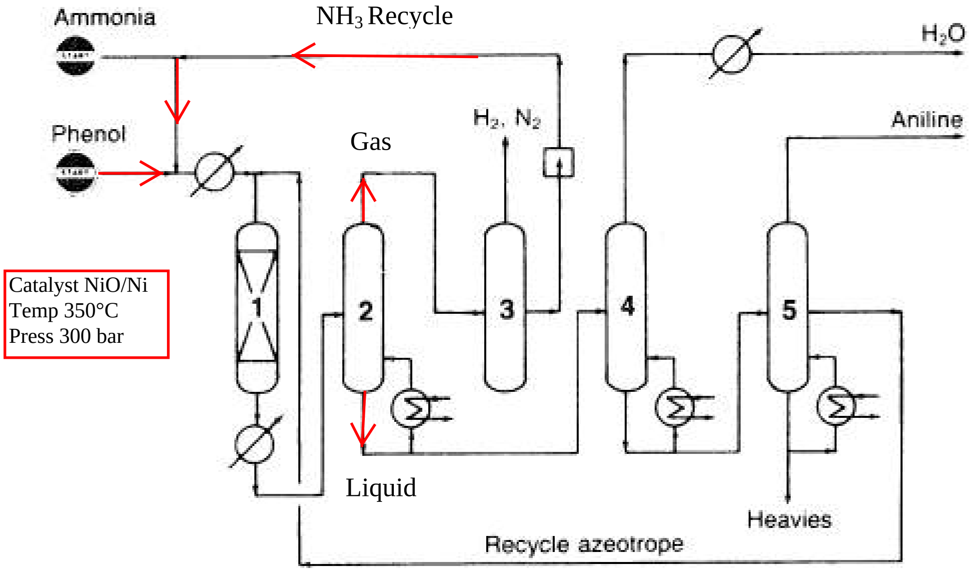
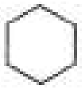
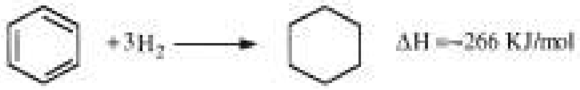


Figure 6-8 The Scientific Co. process for producing aniline from phenol: (1) fixed-bed reactor, (2) liquid-gas separator, (3) ammonia compression and recycling, (4) drier, (5) fractionator.

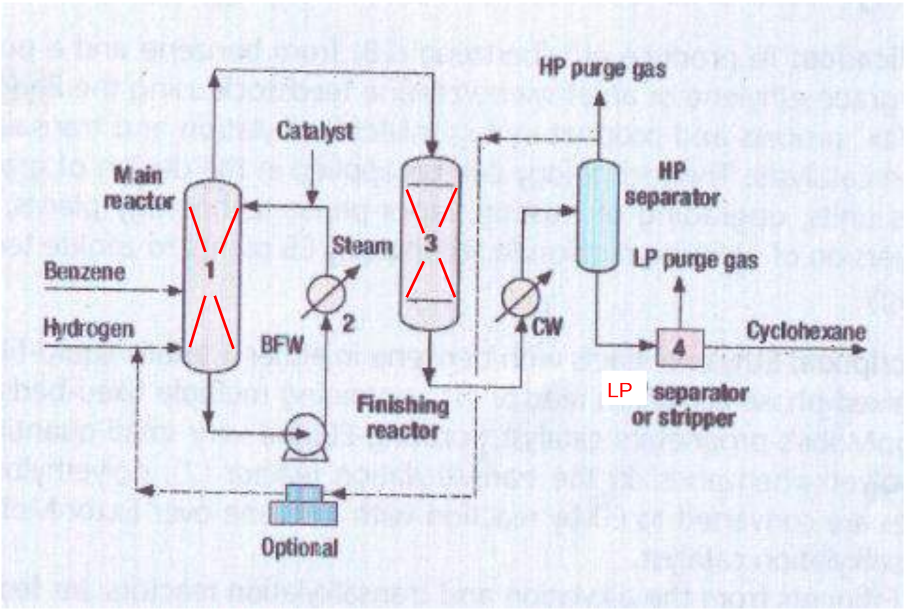
6.2.5 Hydrogenation of Benzene /Cyclohexane



The liquid phase catalytic hydrogenation of benzene produces cyclohexane. Many catalyst systems, such as Ni/alumina and Ni/Pd, are used for the reaction. General reaction conditions are 160-220°C and 25-30 atmospheres. Higher temperatures and pressures may also be used with sulfided catalysts:

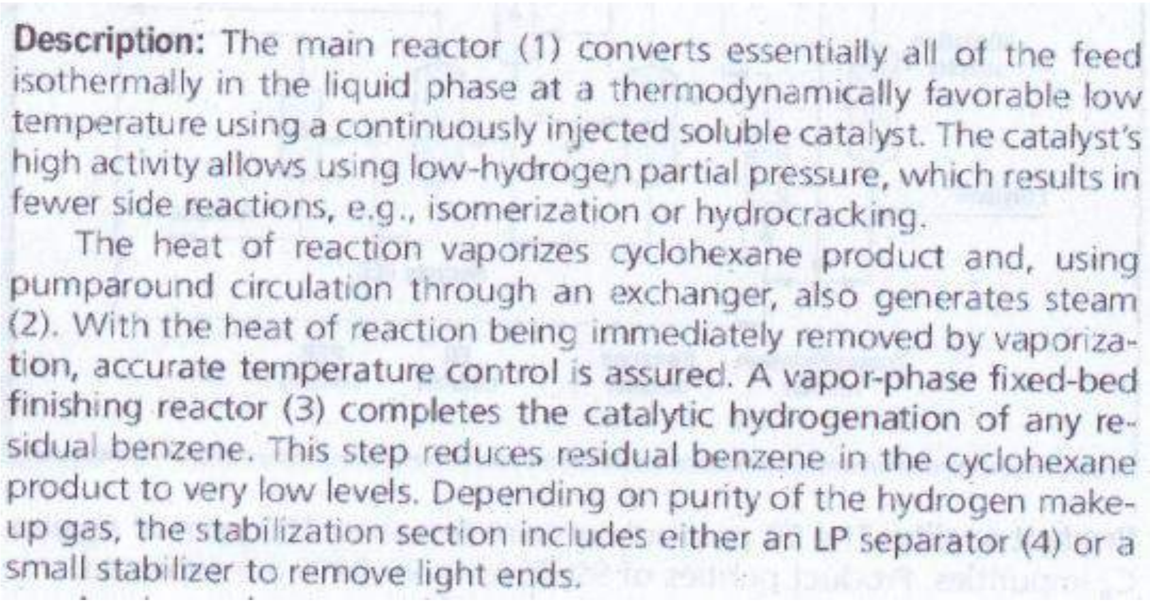


BFW: Back Flow Water
LP: low Pressure
HP: high pressure



HP separator operating at a pressure of 10 – 12 barg, while the LP separator (operating at a pressure of 2.5-3.5 barg)

Figure 6-9. The hydrogenation of benzene to cyclohexane



Description: The main reactor (1) converts essentially all of the feed isothermally in the liquid phase at a thermodynamically favorable low temperature using a continuously injected soluble catalyst. The catalyst's high activity allows using low-hydrogen partial pressure, which results in fewer side reactions, e.g., isomerization or hydrocracking.

The heat of reaction vaporizes cyclohexane product and, using pumparound circulation through an exchanger, also generates steam (2). With the heat of reaction being immediately removed by vaporization, accurate temperature control is assured. A vapor-phase fixed-bed finishing reactor (3) completes the catalytic hydrogenation of any residual benzene. This step reduces residual benzene in the cyclohexane product to very low levels. Depending on purity of the hydrogen make-up gas, the stabilization section includes either an LP separator (4) or a small stabilizer to remove light ends.

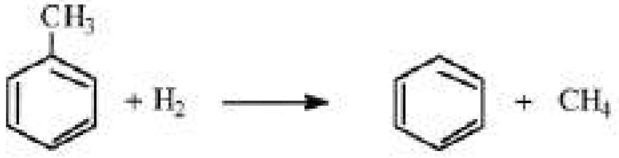
6.3 REACTIONS AND CHEMICALS OF TOLUENE

Toluene (methylbenzene) is similar to benzene as a mononuclear aromatic, but it is more active due to presence of the electron-donating methyl group. However, toluene is much less useful than benzene because it produces more polysubstituted products. Most of the toluene extracted for chemical use is converted to benzene via dealkylation or disproportionation. The rest is used to produce a limited number of petrochemicals.

The main reactions related to the chemical use of toluene (other than conversion to benzene) are the oxidation of the methyl substituent and the hydrogenation of the phenyl group. Electrophilic substitution is limited to the nitration of toluene for producing mononitrotoluene and dinitrotoluenes. These compounds are important synthetic intermediates.

6.3.1 Dealkylation of Toluene

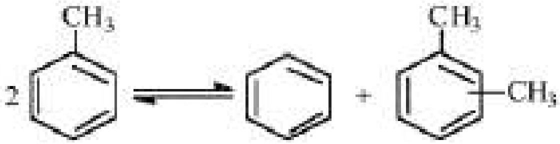
Toluene is dealkylated to benzene over a hydrogenation-dehydrogenation catalyst such as nickel. The hydrodealkylation is essentially a hydrocracking reaction favored at higher temperatures and pressures. The reaction occurs at approximately 700°C and 40 atm. A high benzene yield of about 96% or more can be achieved:



Dealkylation also can be effected by steam. The reaction occurs at 600-800°C over Ni-Cr_2O_3 catalysts, or Ni-Al_2O_3 catalysts at temperatures between 320-630°C. Yields of about 90% are obtained.

6.3.2 Disproportionation of Toluene

The catalytic disproportionation of toluene (Figure 6-10) in the presence of hydrogen produces benzene and a xylene mixture. Disproportionation is an equilibrium reaction with a 58% conversion per pass theoretically possible. The reverse reaction is the transalkylation of xylenes with benzene:



Typical conditions for the disproportionation reaction are 450-530°C and 20 atmospheres. A mixture of $CoO-MoO_3$ on aluminosilicates/alumina catalysts can be used. Conversions of approximately 40% are normally used to avoid more side reactions and faster catalyst deactivation. The equilibrium constants for this reaction are not significantly changed by shifting from liquid to vapor phase or by large temperature changes.

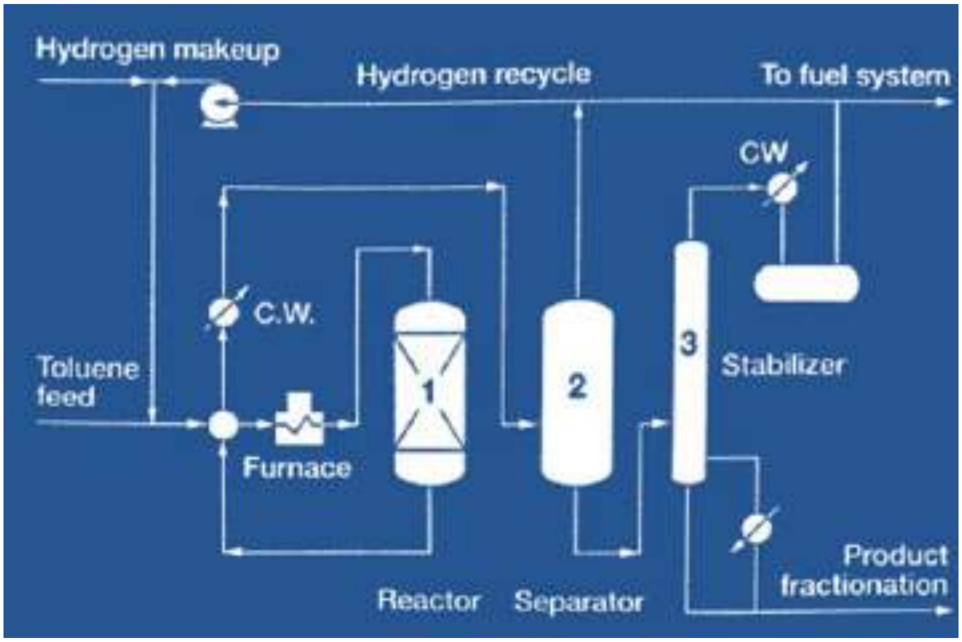
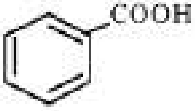


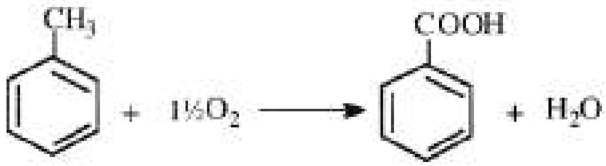
Figure 6-10 The Mobil Oil Corp., IFP process for the disproportionation of toluene to mixed xylenes.

6.3.3 **Oxidation of Toluene**

Benzoic Acid



Oxidizing toluene in the liquid phase over a cobalt acetate catalyst produces benzoic acid. The reaction occurs at about 165°C and 10 atmospheres. The yield is over 90%:



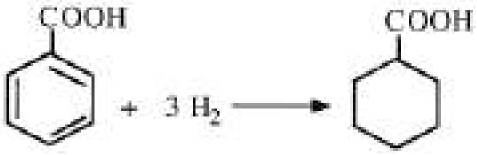
Benzoic acid (benzene carboxylic acid) is a white crystalline solid with a characteristic odor. It is slightly soluble in water and soluble in most common organic solvents. Though much benzoic acid gets used as a mordant in calico printing, it also serves to preserve food, make dentifrices, and kill fungus. Furthermore it is a precursor for caprolactam, phenol, and terephthalic acid.

Caprolactam Production

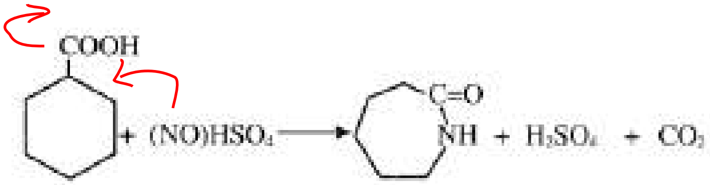
Caprolactam is an organic compound with the formula $(CH_2)_5CONH$. This colorless solid is a lactam of caproic acid (carboxylic acid derived from hexane).

Caprolactam, a white solid that melts at 69°C, can be obtained either in a fused or flaked form. It is soluble in water, ligroin, and chlorinated hydrocarbons. Caprolactam's main use is to produce nylon 6. Other minor uses are as a crosslinking agent for polyurethanes, in the plasticizer industry.

The first step in producing caprolactam from benzoic acid is its hydrogenation to cyclohexane carboxylic acid at approximately 170°C and 16 atmospheres over a palladium catalyst:



In the second step, the resulting acid is then converted to caprolactam through a reaction with nitrosyl-sulfuric acid:



Description

Figure 6-11 shows an integrated caprolactam production process. Toluene, the feed, is first oxidized to benzoic acid. Benzoic acid is then hydrogenated to cyclohexane carboxylic acid, which reacts with nitrosylsulfuric acid yielding caprolactam. Nitrosyl sulfuric acid comes from reacting nitrogen oxides with oleum. Caprolactam comes as an acidic solution that is neutralized with ammonia and gives ammonium sulfate as a by-product of commercial value. Recovered caprolactam is purified through solvent extraction and fractionation.

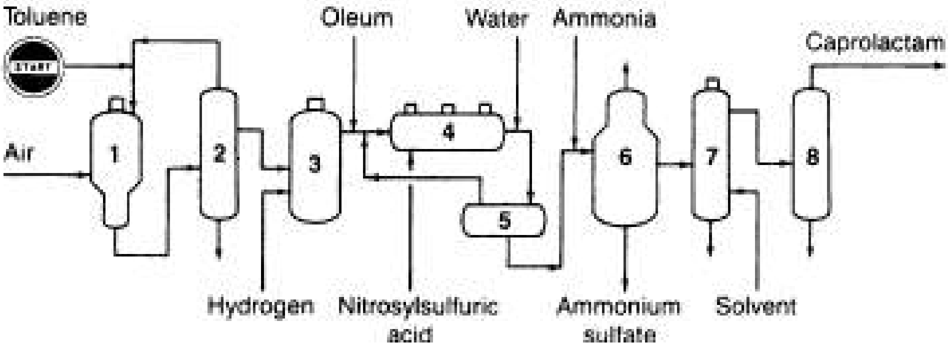
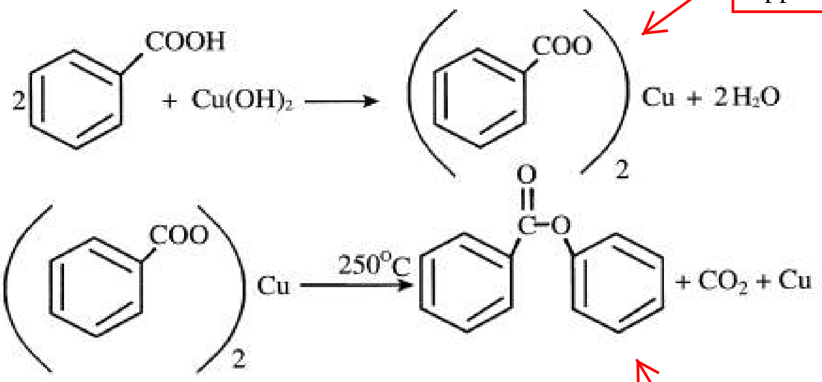


Figure 6-11. The SNIA BPD process for producing caprolactam:(1) toluene oxidation reactor, (2) fractionator, (3) hydrogenation reactor (stirred autoclave), (4) multistage reactor (conversion to caprolactam), (5) water dilution, (6) crystallizer, (7) solvent extraction, (8) fractionator

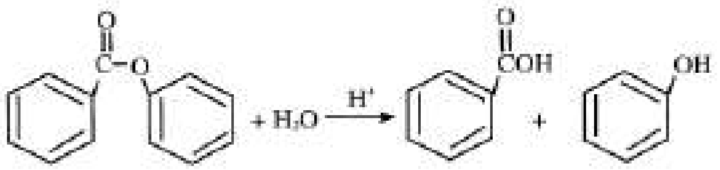
Phenol from Benzoic Acid

The action of a copper salt converts benzoic acid to phenol. The copper reoxidized by air, functions as a real catalyst. The Lummus process operates in the vapor phase at approximately 250°C. Phenol yield of 90% is possible:



copper Benzaote

phenyl benzylacetate



$$Cu + \frac{1}{2}O_2 + H_2O \longrightarrow Cu(OH)_2$$

The overall reaction is

As mentioned before, Phenol can also be produced from chlorobenzene and from cumene, the major route for this commodity, as well as from benzoic acid.

In the Lummus process, the reaction occurs in the liquid phase at approximately 220-240°C over (Mg^{2+} + Cu^{2+}) benzoate. Magnesium benzoate is an initiator, with the Cu^{2+} reduced to Cu^{1+}. The copper (1) ions are reoxidized to copper (II) ions. Figure 6-12 shows the Lummus benzoic-acid-to-phenol process.

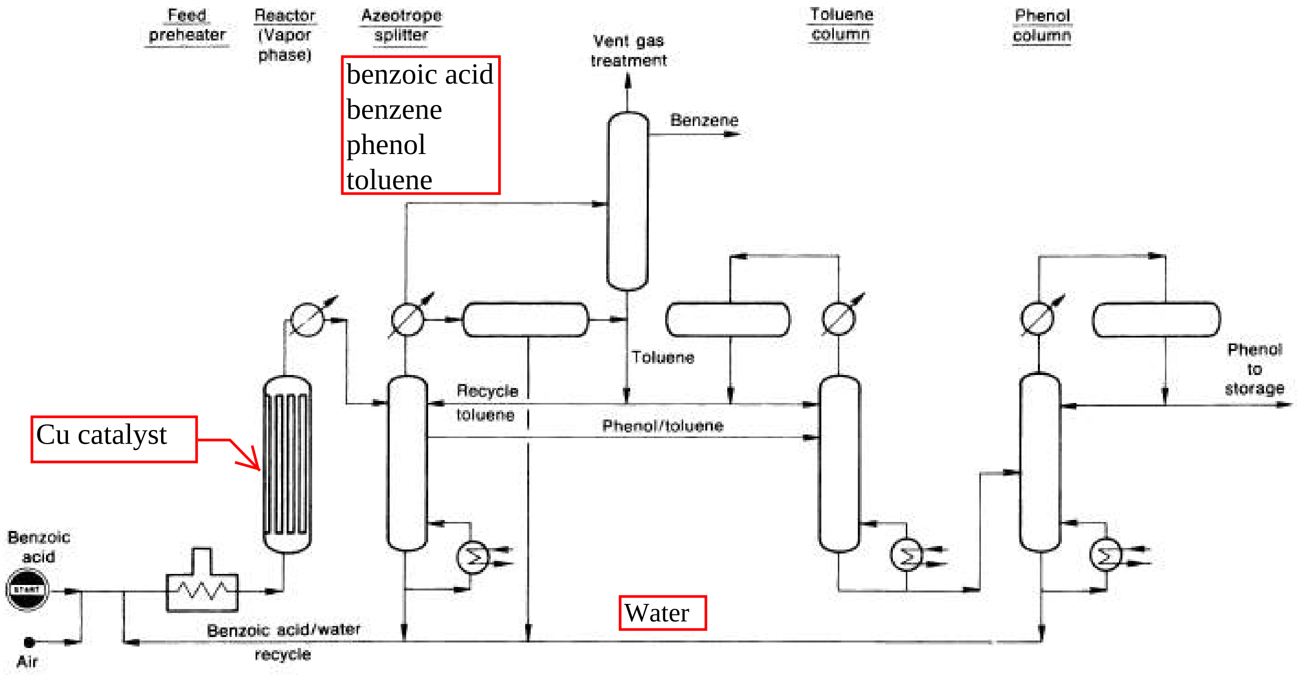
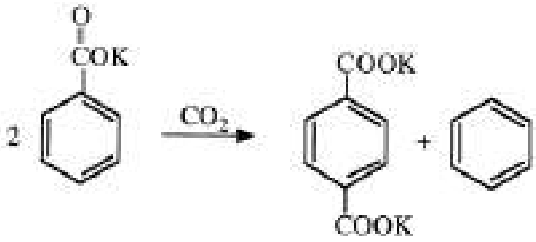


Figure 6-12 The Lummus benzoic-acid-to-phenol process

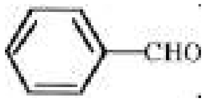
Terephthalic Acid from Benzoic Acid

Terephthalic acid is an important monomer for producing polyesters. The main route for obtaining the acid is the catalyzed oxidation of *para*-xylene. It can also be produced from benzoic acid by a disproportionation reaction of potassium benzoate in the presence of carbon dioxide. Benzene is the co-product:

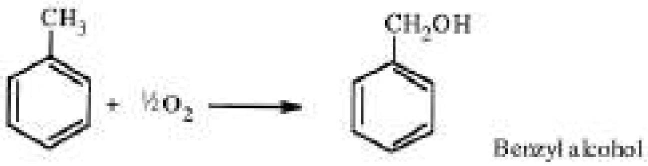


The reaction occurs in a liquid-phase process at approximately 400°C using ZnO or CdO catalysts. Terephthalic acid is obtained from an acid treatment; the potassium salt is recycled.

Benzaldehyde

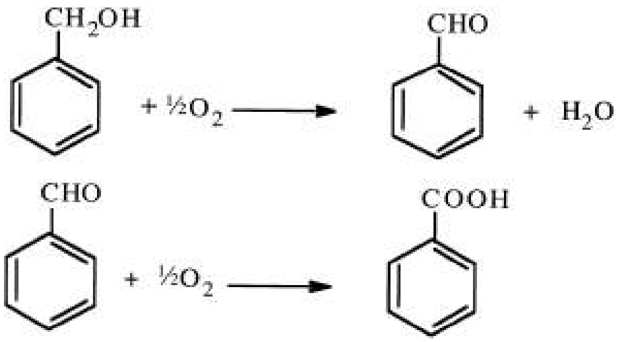


Oxidizing toluene to benzaldehyde is a catalyzed reaction in which a selective catalyst limits further oxidation to benzoic acid. In the first step, benzyl alcohol is formed and then oxidized to benzaldehyde. Further oxidation produces benzoic acid:



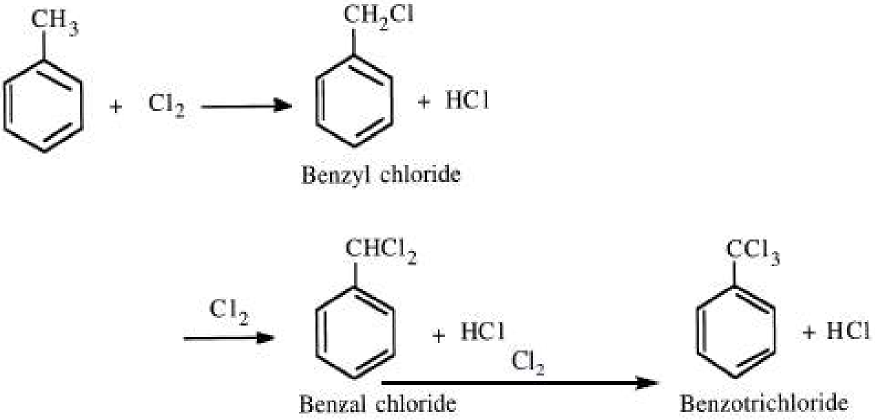
Benzyl structure
$C_6H_5CH_2$–

The problem with this reaction is that each successive oxidation occurs more readily than the preceding one (more acidic hydrogens after introducing the oxygen hetero atom, which facilitates the oxidation reaction to occur). In addition to using a selective catalyst, the reaction can be limited to the production of the aldehyde by employing short residence times and a high toluene/O_2 ratio. In one process, a mixture of UO_2 (93%) and MnO_2 (7%) is the catalyst. A yield of 30–50% could be obtained at low conversions of 10-20%. The reaction temperature is approximately 500°C.

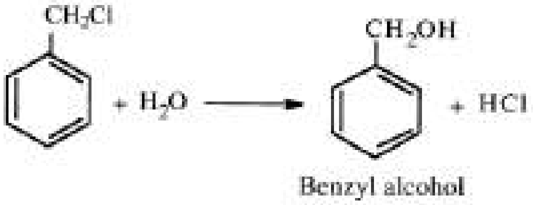


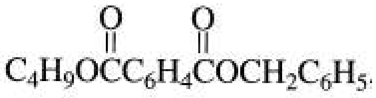
6.3.4 **Chlorination of Toluene**

The chlorination of toluene by substituting the methyl hydrogen is a free radical reaction producing a mixture of three chlorides (benzyl chloride, benzal chloride and benzotrichloride).



The ratio of the chloride mixture mainly derives from the toluene/Cl_2 ratio and the contact time. Benzyl chloride is produced by passing dry chlorine into boiling toluene (110°C) until reaching a density of 1.283. At this density, the concentration of benzyl chloride reaches the maximum. Light can initiate the reaction. Benzyl chloride can produce benzyl alcohol by hydrolysis:





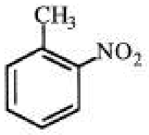
$C_4H_9O\overset{O}{\overset{\|}{C}}C_6H_4\overset{O}{\overset{\|}{C}}OCH_2C_6H_5$.

Benzyl alcohol is a precursor for butylbenzyl phthalate and vinyl chloride plasticizer.

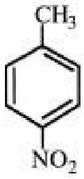
Benzyl chloride is also a precursor for phenylacetic acid via the intermediate benzyl cyanide. Phenylacetic acid is used to make phenobarbital (a sedative) and penicillin G. Benzal chloride is hydrolyzed to benzaldehyde, and benzotrichloride is hydrolyzed to benzoic acid. Chlorinated toluenes are not large-volume chemicals, but they are precursors for many synthetic chemicals and pharmaceuticals.

6.3.5 **Nitration of Toluene**

Nitration of toluene is the only important reaction that involves the aromatic ring rather than the aliphatic methyl group. The nitration reaction occurs with an electrophilic substitution by the nitronium ion. The reaction conditions are milder than those for benzene due to the activation of the ring by the methyl substituent. A mixture of nitrotoluenes results. The two important monosubstituted nitrotoluenes are *o*- and *p*-nitrotoluenes:

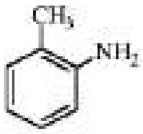


o-Nitrotoluene

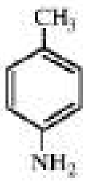


p-Nitrotoluene

Mononitrotoluenes are usually reduced to corresponding toluidines, which make dyes and rubber chemicals:

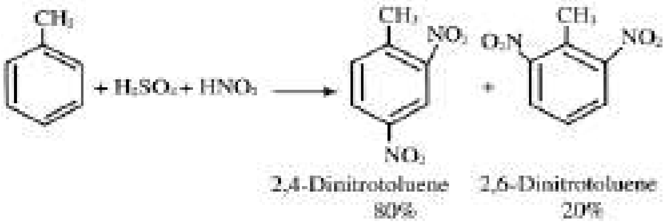


o-Toluidine

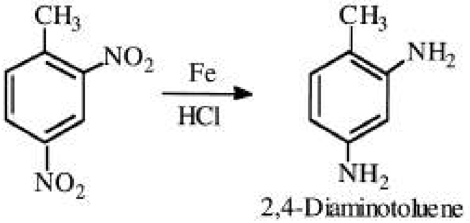


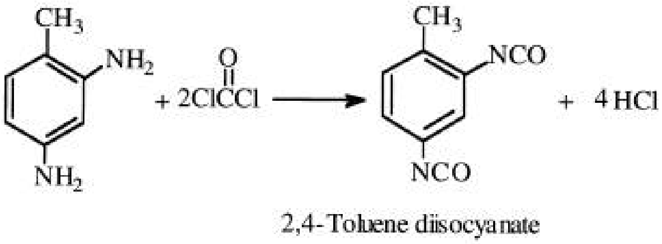
p-Toluidine

Dinitrotoluenes are produced by nitration of toluene with a mixture of concentrated nitric and sulfuric acid at 80°C. The main products are 2,4- and 2,6-dinitrotoluenes:



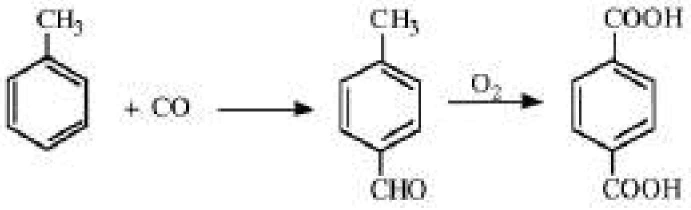
The dinitrotoluenes are important precursors for toluene diisocyanates (TDI), monomers used to produce polyurethanes. The TDI mixture is synthesized from dinitrotoluenes by a first-step hydrogenation to the corresponding diamines. The diamines are then treated with phosgene ($COCl_2$) to form TDI. The yield from toluene is approximately 85%:





6.3.6 Carbonylation of Toluene

The carbonylation reaction of toluene with CO in the presence of HF/BF_3 catalyst produces p-tolualdehyde. A high yield results (96% based on toluene). *p*-Tolualdehyde could be further oxidized to terephthalic acid, an important monomer for polyesters:



p-Tolualdehyde is also an intermediate in the synthesis of perfumes, dyes and pharmaceuticals.

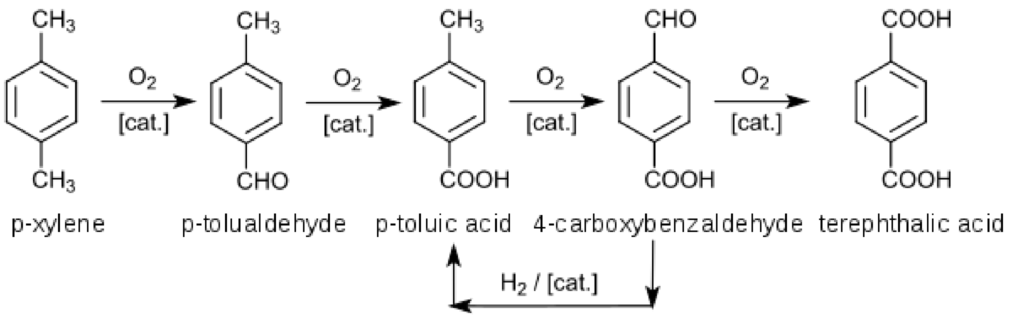
6.4 REACTIONS AND CHEMICALS OF XYLENES

Xylenes (dimethylbenzenes) are an aromatic mixture composed of three isomers (*o*-, *m*-, and *p*-xylene). They are normally obtained from catalytic reforming and cracking units with other C_6, C_7, and C_8 aromatics. Separating the aromatic mixture from the reformate is done by extraction-distillation and isomerization processes.

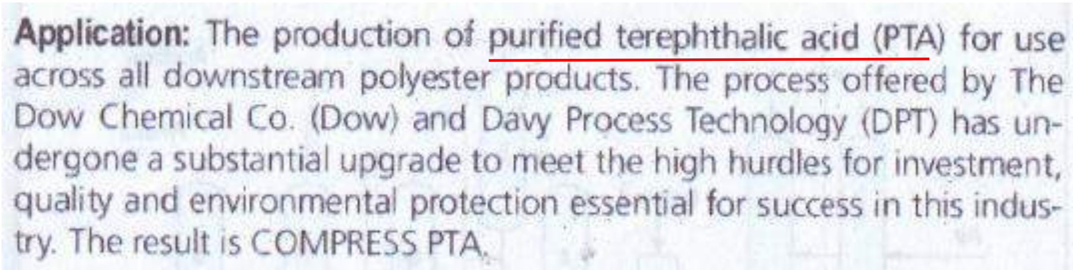
para-Xylene is the most important of the three isomers for producing terephthalic acid to manufacture polyesters. m-Xylene is the least used of the three isomers, but the equilibrium mixture obtained from catalytic reformers has a higher ratio of the meta isomer. *m*-Xylene is usually isomerized to the more valuable *p*-xylene.

Terephthalic acid ($HOOCC_6H_4COOH$)

The catalyzed oxidation of p-xylene produces terephthalic acid (TA). Cobalt acetate promoted with either NaBr or HBr is used as a catalyst in an acetic acid medium. Reaction conditions are approximately 200°C and 15 atmospheres. The yield is 95%:



Special precautions must be taken so that the reaction does not stop at the p-toluic acid stage. Figure 6-13 shows a typical p-xylene oxidation process to produce purified terephthalic acid (PTA).



Application: The production of purified terephthalic acid (PTA) for use across all downstream polyester products. The process offered by The Dow Chemical Co. (Dow) and Davy Process Technology (DPT) has undergone a substantial upgrade to meet the high hurdles for investment, quality and environmental protection essential for success in this industry. The result is COMPRESS PTA.

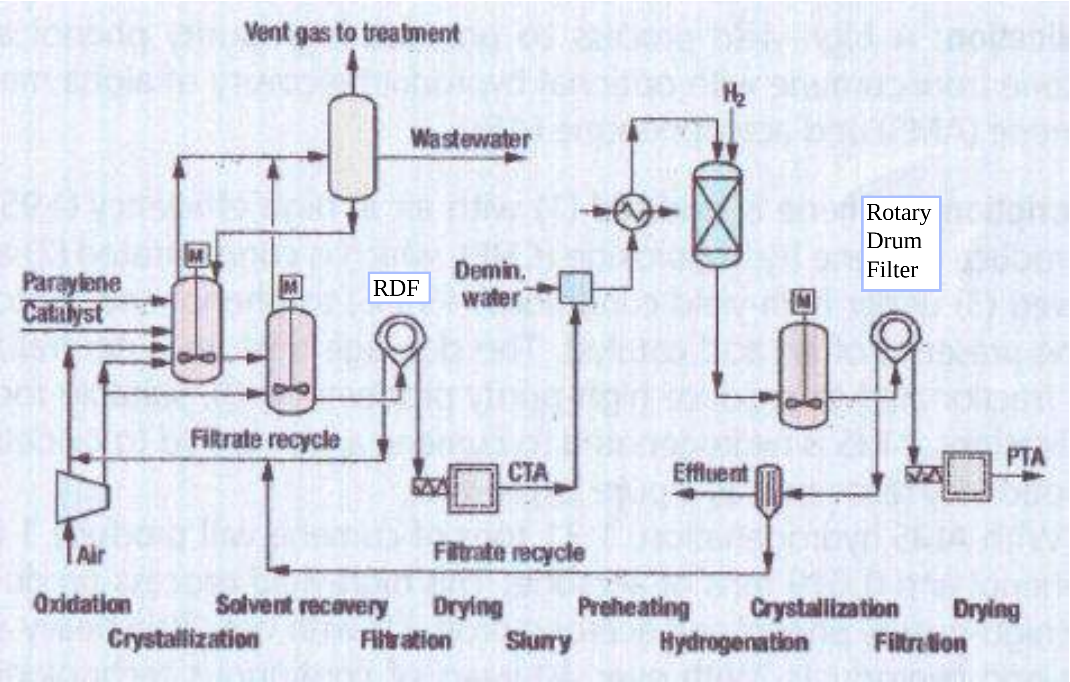
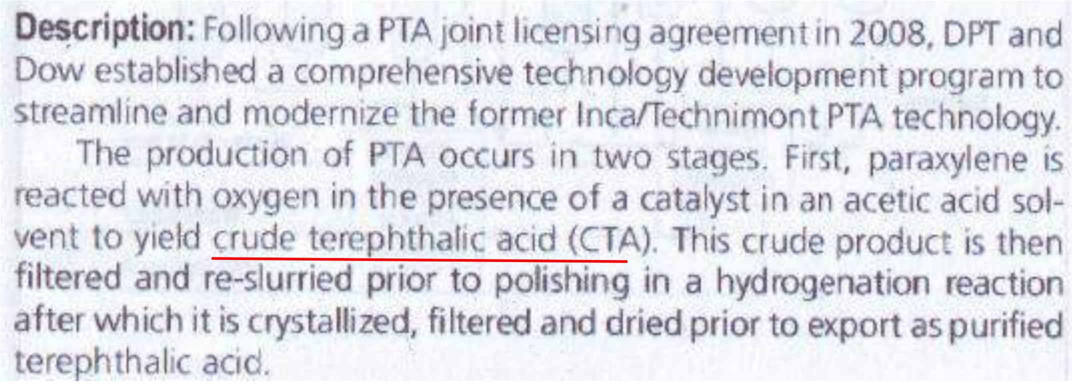


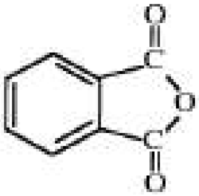
Figure 6-13 A typical p-xylene to purified terephthalate acid process.



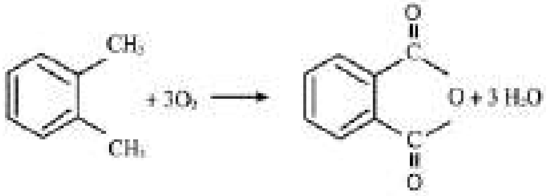
Description: Following a PTA joint licensing agreement in 2008, DPT and Dow established a comprehensive technology development program to streamline and modernize the former Inca/Technimont PTA technology.

The production of PTA occurs in two stages. First, paraxylene is reacted with oxygen in the presence of a catalyst in an acetic acid solvent to yield crude terephthalic acid (CTA). This crude product is then filtered and re-slurried prior to polishing in a hydrogenation reaction after which it is crystallized, filtered and dried prior to export as purified terephthalic acid.

Phathalic Anhydride



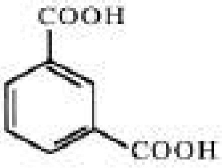
Currently, phthalic anhydride is mainly produced through catalyzed oxidation of o-xylene. A variety of metal oxides are used as catalysts. A typical one is V_2O_5 + TiO_2/Sb_2O_3. The conditions for the vapor-phase oxidation are 375-435°C and 0.7 atm. The yield of phthalic anhydride is about 85%:



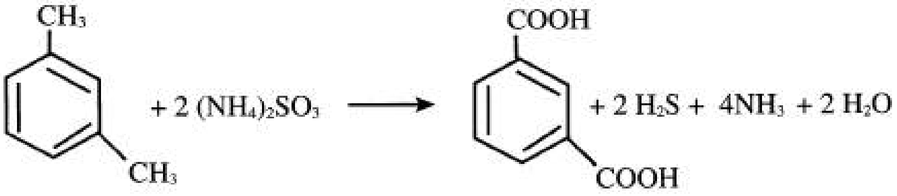
Liquid-phase oxidation of o-xylene also works at approximately 150°C. Cobalt or manganese acetate in acetic acid medium serves as a catalyst. The major by-products of this process are maleic anhydride, benzoic acid, and methylmaleic anhydride. Phthalic anhydride's main use is for producing plasticizers by reactions with C_4-C_{10} alcohols.

Phthalic anhydride is also used to make polyester and alkyd resins. It is a precursor for phthalonitrile by an ammoxidation route used to produce phthalamide and phathilimide.

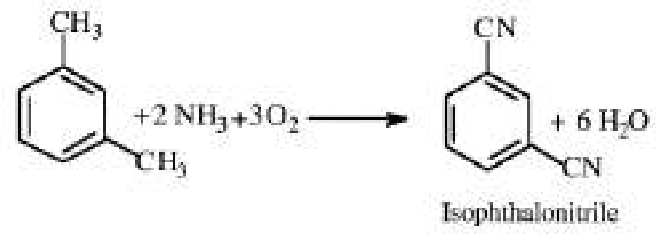
Isophthalic Acid



The oxidation of m-xylene produces isophthalic acid. The reaction occurs in the liquid-phase in presence of ammonium sulfite:



Isophthalic acid's main use is for producing polyesters that are characterized by a higher abrasion resistance than those using other phthalic acids. Polyesters from isophthalic acid are used for pressure molding applications. Ammoxidation of isophthalic acid produces isophthalonitrile. The reaction resembles the one used for ammoxidation of phthalic anhydride:



Isophthalonitrile serves as a precursor for agricultural chemicals. It is readily hydrogenated to the corresponding diamine, which can form polyamides or be converted to isocyanates for polyurethanes.